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Externally Tunable Dynamic Confinement Effect in Organosilica Sol−Gels

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Molecules tend to behave differently when placed in confined spaces. Confinement of molecules in nanoscale enclosures results in drastic alterations in physical and chemical properties.[1] Such an effect is exploited by nature to utilize the ordered nanostructure afforded by cellular organization[2] and emulated in synthetic porous systems to alter structure and reactivity of molecules.[3] However, these systems are characterized by spatially fixed cavities such that encapsulated molecules experience an environment that is constant, and once encapsulated in the porous structure the environment remains largely unchanged and spatial modulation is not feasible. Consequently, systems wherein dimensions of the pores can be externally modulated by means of an externally applied stimulus provide a pathway to the design of smart systems with externally tunable spatial confinement effects.

In this context, large changes in spatial conformations under confinement have been postulated as the basis for the stabilization of protein folding pathways mediated by chaperonin cavities.[4] While the stabilization of proteins has been achieved upon confinement in pores and cavities,[5] the ability of chaperonins to effectively modulate the confinement effect via dynamic changes in spatial conformations and pore volume[6] remains unparalleled, and artificial analogues capable of such tunable confinement effect remain desirable. With this in mind, we report the unique temperature dependent order−disorder processes occurring in the pores of an organosilica sol−gel system made from the hydrolysis of bis[3-(trimethoxysilyl)propyl] ethylenediamine (enTMOS) precursor. We show that these porous glasses act as thermoresponsive materials, which undergo reversible changes in pore volume resulting in the dynamically altered confinement of encapsulated entities as manifested by the synchronously correlated luminescence of the encapsulated entity. A particularly remarkable feature of this system is that the temperature-dependent confinement effect provided by the gels is reversible and can be efficiently modulated by simply changing the temperature. We have recently demonstrated variations in molecular selectivity as well as bulk volume changes of organically modified silica gels by means of temperature.[7] Here, we show that the porous sol−gels exhibit dynamic changes in pore volumes with pore shrinkage at high temperature and pore enlargement at low temperature[7a] thereby enabling spatial modulation of the nanoenvironment of encapsulated luminescent probe entities.

Optical probes of structure, organization, and confinement have been extensively used to elucidate changes occurring along the sol−gel−xerogel structural transformations.[8] The luminescence of anilinonaphthalenesulfonate (ANS) dyes is dependent upon spatial changes in their environment, particularly confinement effects, and has been extensively used to monitor environmental changes associated with order−disorder phenomena in membranes, gels, and other systems.[9] In this study, we use ANS as a probe to show that its luminescence is characterized by a strong correlation with changes in pore volume of sol−gels because of loss of solvent. To monitor the confinement effect, the ammonium salt of 8-anilino-1-naphthalenesulfonic acid was used because of its solubility in water/methanol mixtures. A 3 mM stock solution of ANS was made by dissolving 0.0047 g of the dye in a solvent mixture composed of 1 mL methanol and 4 mL water. The volume sensitive gels used in this study were prepared from a sol made by mixing 1.0 mL of enTMOS, 1.0 mL of methanol, and 2.0 mL of 3 mM stock solution of ANS. The resulting sol was coated onto a precleaned glass slide with the approximate dimensions of 0.9 cm × 3 cm. The slides were allowed to dry for 30 min under a nitrogen environment and then were placed in a quartz cuvette. The cuvette was filled with 4 mL of 4:1 water/methanol mixture containing water purged with nitrogen for 4 h, and the cuvette was sealed under nitrogen prior to measurements. The glass slides in the sealed cuvette were used for all the luminescence measurements with an excitation wavelength of 370 nm. A similar procedure was followed with control sol−gels made with tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMOS), and 3-aminopropyltrimethoxysilane (APTS). The TMOS−MTMOS sol was made by mixing 1.5 mL of TMOS, 1.5 mL of MTMOS, 0.8 mL of water, 1.0 mL of methanol, and 0.044 mL of 0.04 M HCl followed by sonication for 40 min. An amount of 1 mL of this sol was mixed with 1 mL of the ANS stock solution to form gel films on a glass slide. Similarly, the APTS−MTMOS sol was made by mixing 1.5 mL of APTS, 1.5 mL of MTMOS, 0.8 mL of water and 1.0 mL of methanol. An amount of 1 mL of this sol was mixed with 1 mL of ANS stock solution to form the gel on a glass slide. For solution measurements, 1.5 mM ANS solution made in a water−methanol mixture was used.

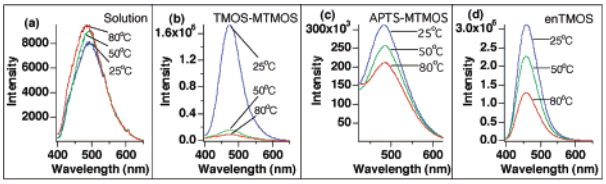

Figure 1. Luminescence spectra of ANS at 25 °C, 50 °C, and 80 °C in different environments: (a) solution, (b) TMOS−MTMOS, (c) APTS−MTMOS, and (d) enTMOS.

The luminescence spectra of ANS in different environments as a function of changing the temperature are shown in Figure 1. There is slight but distinct increase in luminescence intensity of ANS in the water/methanol solution (Figure 1a) possibly because of reduced microviscosity leading to a disorganization of solvent shell around the molecule as the temperature is increased.[10] On the other hand, the luminescence intensity decreases (Figures 1b−d) considerably in the sol−gel matrixes as the temperature is increased from 25 to 80 °C because of the decrease in pore sizes resulting from condensation of the gel network. It is important to note that similar changes in luminescence are also observed when the gels are ambiently dried for an extended period. Overall, the results indicate a strong sensitivity of the ANS molecule to changes in its immediate environment caused by confinement effect owing to expulsion of

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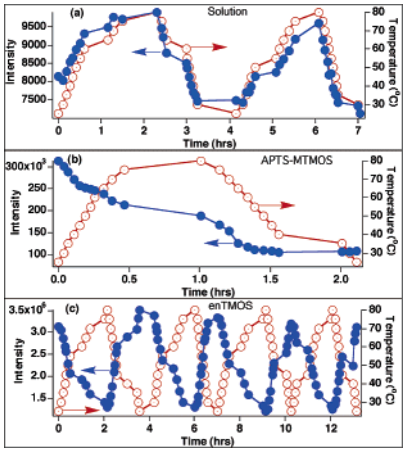

Figure 2. Changes in luminescence intensity of ANS (−●−) owing to sequential variations in temperature (−⊙−) in different environments: (a) solution, (b) APTS−MTMOS, and (c) enTMOS.

solvent and consequent pore shrinkage and confirm changes in luminescence intensity as a sensitive indicator of the confinement effect.

Next, we investigated the changes in luminescence intensity of ANS as a function of cyclical variation of temperature between 25 and 80 °C. The results are shown in Figure 2. While there is a slight change in intensity in solution medium (Figure 2a) which correlates directly with temperature, the control sol−gel samples TMOS−MTMOS (data not shown) and APTS−MTMOS (Figure 2b) show an irreversible decrease in intensity as a function of time independent of temperature. This is consistent with the fact that in these gels, the pores continue to shrink irreversibly along with the expulsion of solvent as a result of ongoing hydrolysis and condensation reactions. On the other hand, in enTMOS sol−gels (Figure 2c), the intensity exhibits an inverse correlation with temperature such that a decrease in intensity accompanies an increase in temperature. When the temperature is lowered, the intensity increases and returns to original value. As shown in Figure 2c, these temperature dependent changes in intensity are reversible and can be observed for several cycles.[11] Thus, the results indicate reversible changes in the nanoenvironment of ANS caused by dynamic changes in pore sizes owing to the sequential expulsion/intake of solvent from the enTMOS gels during cyclical temperature changes.

Taken together, the results suggest a unique temperature-controlled spatial modulation of the ANS nanoenvironment within enTMOS sol−gels owing to its unique ability to exhibit volume transitions in response to temperature changes.[7a−b] The luminescence of ANS is governed by changes in microenvironment, conformational changes, and specific solute−solvent interactions. To a first approximation, the altered interactions of ANS with the enTMOS gels may be one of the causes of the observed changes in luminescence intensities as the pores exhibit dynamic volume changes. The differential conformations and variations in specific solute−solvent interactions of ANS in enlarged versus shrunk pores may be other factors that contribute to these changes as the nanoenvironment of ANS is varied because of the dynamic confinement effect. While details of the complex interplay of structure and dynamics in these systems that govern the precise nature of interactions between ANS and the sol−gels remain to be understood and comprise the future scope of this work, overall, the variations in intensity are consistent with the confinement of an ANS molecule resulting from pore size variations during thermal changes. The results conclusively establish the dynamic nature of the spatial environment experienced by ANS in the pores of enTMOS induced by expulsion/intake of solvent from the pores. Furthermore, the results indicate the dynamic volume changes of enTMOS gels because of the presence of the bispropyl ethylenediamine group, which is found to be a critical requirement for the gels to exhibit reversible changes in porosity, since sol−gels that do not contain this group exhibit irreversible pore shrinkage. In this context, it is important to note that even the structurally analogous APTS−MTMOS gels exhibit irreversible pore collapse. Thus, it is clearly evident that the volume sensitivity of the gels is exclusively due to the presence of the $Si-(CH_2)_3-NH-(CH_2)_2-NH-(CH_2)_3-Si$ group, and gels that lack this functionality do not exhibit dynamic changes in pore volumes. Additionally, the fact that the nanoenvironment of ANS in enTMOS gels can be reversibly altered by simply changing the temperature (with all other conditions remaining constant) indicates that the confinement effect is strongly coupled with the thermoresponsivity of the materials and the concomitant changes in porosity. As such, the observed results are consistent with the dynamic confinement originating as a result of variations in thermally regulated order−disorder processes.

In conclusion, our results establish the ability of enTMOS sol−gels to exhibit thermally regulated changes in pore volumes resulting in dynamic confinement of encapsulated entities. The enTMOS gels undergo temperature-controlled variations in porosity, which allow a fine-tuning of the spatial dimensions in the environment of encapsulated molecules leading to a thermoregulated dynamic confinement effect. Such a modulation of interactions is quite reminiscent of the chaperonin function in biology wherein allosteric regulation of interactions creates a spatially modulated nanocavity, which can exhibit dynamic changes in pore volume to facilitate protein folding. This feature will likely find potential applications in dynamically controlling the structure and reactivity of encapsulated molecules as well as in designing novel materials with dynamically regulated photonics.

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(11) There was no leaching of ANS from the gels to external solvent during the time course of the experiments. This was confirmed by recording the spectra of the external solution at the end of all the experiments.

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